Theoretical determination of the exchange coupling constants of a single-molecule magnet Fe_{10} complex

Gopalan Rajaraman [1], Eliseo Ruiz *, Joan Cano [2], Santiago Alvarez

Departament de Química Inorgànica and Centre de Recerca en Química Teòrica Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Abstract

Theoretical methods based on density functional theory have been employed to analyze the exchange interactions in an Fe_{10} complex. The calculated exchange coupling constants are in excellent agreement with those obtained previously by fitting the experimental data using classic Monte-Carlo simulations. The relative stabilities of the spin states obtained by a diagonalization of the matrix Hamiltonian using the Lanczos algorithm have been studied. These results show that the S value of the ground state is extremely sensitive to the J values, thus, a very small change of the exchange coupling constants could modify the total spin of the molecule.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Some polynuclear transition metal complexes present slow relaxation of their magnetization at low temperature and they have been named single-molecule magnets (SMM) [1,2]. These systems also present thermally assisted quantum tunneling processes, making them interesting for quantum computing. Such molecules are also good candidates for the storage of information at the molecular level if the thermal jump of the barrier and the crossing through quantum tunneling can be avoided. The energy corresponding to the barrier is equal to $D \cdot S^2$, D being the zero-field splitting parameter and S the total spin of the molecule. Thus, the requirements for such systems to have a high barrier are a large ground state spin and a large negative magnetic anisotropy. The first single-molecule magnet reported was the $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ complex, usually known as Mn_{12} [3]. Several single-molecule magnets have been

characterized to date, but among them the most widely studied complex besides Mn_{12} is the Fe_8 system, $[Fe_8O_8(OH)_{12}(tacn)_6]Br_8 \cdot 9H_2O$ (tacn = 1,4,7-triazacyclononane), both with $S = 10$ [4,5]. Benelli et al. have reported an Fe_{10} complex with $S = 11$ that presents below 1 K a frequency-dependence of the out-of-phase AC magnetic susceptibility vs. temperature plot, a characteristic feature of the SMM systems, with an estimated energy barrier of 5.3 K [6,7]. This compound of formula $[Fe_{10}Na_2(O)_6(OH)_4(O_2CPh)_{10}(chp)_6(H_2O)_2(Me_2CO)_2]$ (chp = 6-chloro-2-pyridonato) adopts a cage structure (see Fig. 1). Previously, in order to obtain the exchange coupling constants Benelli et al. have performed a study by fitting the experimental magnetic susceptibility using classic Monte-Carlo simulations [7].

Up to now, there are few examples in the literature of theoretical studies of this kind of systems, most of them have been devoted to the Mn_{12} and Mn_4 complexes [8–11] and the V_{15} complex [12,13]. In our research group, we have focused our studies on polynuclear Fe^{III} complexes, such as Fe_{19} [14], Fe_8 and Fe_{11} complexes [15,16] and a recent review covering this kind of theoretical studies can be found in [17]. The aim of this communication is to report a study of the J values in this Fe_{10} complex using methods based on density functional

---

* Corresponding author. Fax: +93 490 77 25.
  E-mail address: eliseo.ruiz@qi.ub.es (E. Ruiz).
[1] Permanent address: Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom.
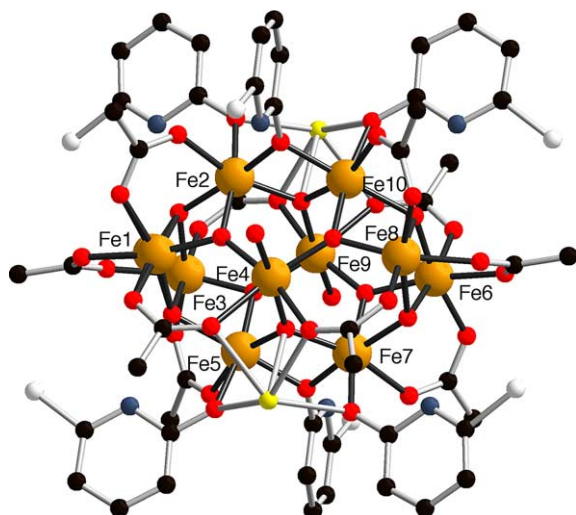[2] Institució Catalana de Recerca i Estudis Avançats (ICREA).

Fig. 1. Representation of the molecular structure of the Fe_{10} complex $[Fe_{10}Na_2(O)_6(OH)_4(O_2CPh)_{10}(chp)_6(H_2O)_2(Me_2CO)_2]$ (chp = 6-chloro-2-pyridonato). The nitrogen, oxygen, iron, carbon, and hydrogen atoms are represented by spheres of different shades of gray, from dark to bright, respectively.

theory. Subsequently, we will analyze the relative energies of the ground and first excited states for the different sets of exchange coupling constants obtained. For this purpose, due to the impossibility to perform a full diagonalization due to the large size of the Hamiltonian matrix, we will employ a Lanczos algorithm that allows one to obtain only the energies corresponding to the lowest states.

2. Results and discussion

The spin Hamiltonian considering only the exchange coupling terms can be expressed as:

$$\hat{H} = -J_1[\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_3\hat{S}_5 + \hat{S}_5\hat{S}_7 + \hat{S}_6\hat{S}_7 + \hat{S}_6\hat{S}_8$$
$$+ \hat{S}_8\hat{S}_{10} + \hat{S}_2\hat{S}_{10}] - J_2[\hat{S}_1\hat{S}_5 + \hat{S}_2\hat{S}_3 + \hat{S}_6\hat{S}_{10}$$
$$+ \hat{S}_7\hat{S}_8] - J_3[\hat{S}_4(\hat{S}_1 + \hat{S}_2 + \hat{S}_5 + \hat{S}_7 + \hat{S}_8 + \hat{S}_{10})$$
$$+ \hat{S}_9(\hat{S}_2 + \hat{S}_3 + \hat{S}_5 + \hat{S}_6 + \hat{S}_7 + \hat{S}_{10})], \quad (1)$$

where $\hat{S}_i$ are the spin operators of each paramagnetic Fe^{III} center. We consider only three different exchange coupling constants (as done in the original Letter containing the experimental data) [7] despite that, for instance, J corresponds to four slightly different exchange pathways, as we will discuss later. A detailed description of the procedure used to obtain the exchange coupling constants can be found in [8,9] and a description of the computational details is provided in Section 3.

The calculated exchange coupling constants are presented in Table 1. The large size of the Hamiltonian matrix ($6^{10} = 6.85 \times 10^7$) corresponding to the Fe_{10} complex

makes it impossible to perform a fitting using the exact diagonalization of the measured magnetic susceptibility to obtain the three different J values (see Eq. (1) and Fig. 1) as usually done for smaller molecules. Hence, Benelli et al. have performed a fitting of the experimental data employing classic Monte-Carlo simulations (J_{MC} in Table 1) [7]. We obtain an excellent agreement between the two sets of calculated J values and those obtained from the fitting procedure based on Monte-Carlo simulations. It is worth noting that our results allowed us to detect that the J_1 and J_3 values in [7] were interchanged. The calculated values show two trends that were previously found for Fe_{14} and Fe_{19} complexes [14,18]: (i) the single μ_3-O bridges (J_3) usually provide the strongest coupling, (ii) double or triple bridges as those corresponding to the J_1 interaction usually result in weaker interactions than those provided by single bridges. In this case, due to the low symmetry of the molecule, there are four different exchange pathways corresponding to the J_1 interaction (notice the four different Fe···Fe distances), three of them are different not only in structure but also in the bridging ligands (see Table 1).

We wish now to check the ability of the different sets of J values to reproduce the spin of the ground state. Hence, in order to determine the total spin of the ground state for the four different sets of J values by using the diagonalization of the Heisenberg Hamiltonian matrix, we have employed the Lanczos algorithm [19], because the exact diagonalization approach is unsuitable due to the large number of states. The results are indicated in Table 1. It is worthwhile noting that the lowest energy states are very close in energy due to the complexity of the system and to the presence of spin frustration in some interactions. This fact makes this kind of complexes especially challenging as far as the accuracy of the obtained J values is concerned. Thus, despite the good agreement between the four sets of J values, three of them do not reproduce correctly the total spin of the ground state ($S = 11$). The accuracy needed to reproduce the value of the total spin is not achieved in this case even by using the fitting based on Monte-Carlo simulations. One of the drawbacks of the Classical Monte-Carlo methods is the non-accurate description of the magnetic susceptibility curve at low temperature, thus resulting in an incorrect value of the spin at low temperature [20]. However, simply introducing a very small change from the fitted J values to obtain the J_S set (see Table 1), we can correctly reproduce the total spin. The small change introduced in the two smallest J values of the J_S set has a dramatic effect on the relative stability of the states, as shown in Fig. 2, giving the right total spin value $S = 11$. A similar case has been encountered in an Fe_{14} complex [18], although the estimation of the ground state for the given set of J values was not possible due to the use of classical Monte-Carlo simulations. Here, we show that the use of the Lanczos algorithm is

Table 1
Description of the bridging ligands, average Fe···Fe distances and bond angles and calculated exchange coupling constants J (cm^{-1}) for the Fe$_{10}$ complex

	Bridging ligands	d(Fe···Fe) (Å)	J_{PBE}	J_{B3LYP}	J_{MC}[a]	J_S
J_1	(μ_3-O)(μ-OClpy)	3.001	-8.4	-11.0	-10.0	-9.0
	(μ_3-O)(μ_3-OH)(μ-OOCCH$_3$)	2.974, 2.976				
	(μ_3-OH)$_2$(μ-OOCCH$_3$)	3.127				
J_2	(μ_3-OH)	3.665, 3.673	-12.9	-13.2	-13.0	-12.0
J_3	(μ_3-O)	3.471, 3.456, 3.463 3.496, 3.447, 3.458	-49.3	-61.7	-44.0	-44.0
S_{GS}			13	12	10	11
S_{ES}			14	13	11	10
$E_{GS} - E_{ES}$			4.2	0.7	5.7	2.8

The J values were calculated with the PBE and B3LYP functionals using numerical and Gaussian functions, respectively. The results obtained from a fitting of the experimental magnetic susceptibility curve are also indicated (J_{MC})[a]. The set of J values labeled as J_S corresponds to a case that reproduces correctly the ground state of the molecule. The S_{GS} and S_{ES} values are the total spin of the ground and first excited states corresponding to each set of J values and $E_{GS} \times E_{ES}$ (in cm^{-1}) is the energy difference between those states.

[a] The reader must be warned that in [7] the J_1 and J_3 values are interchanged.
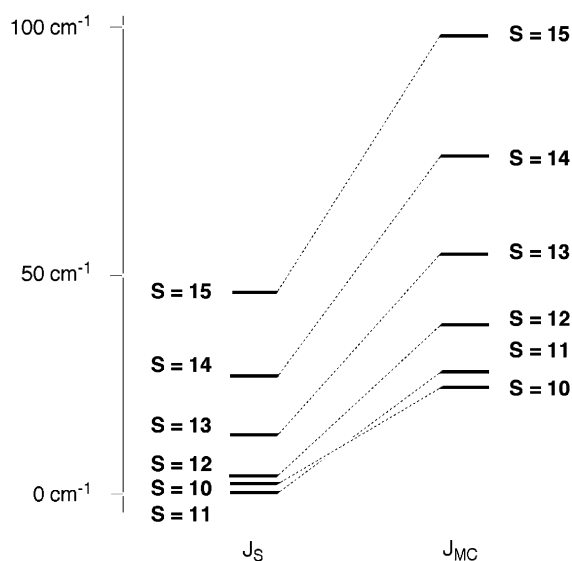

Fig. 2. Lowest energy levels of the ground and excited states for each spin value corresponding to the J_{MC} and J_S sets of exchange coupling constants.

very helpful to obtain information about the ground state, which is necessary to gain confidence in the sign and magnitude of the calculated J values.

After these results, we must be aware that the fitting procedures and, in general, all kind of simulations and determinations of J values must be done carefully, especially in systems with spin frustration, verifying that the total spin of the ground state is correctly reproduced.

3. Computational details

Electronic structure calculations have been performed with the GAUSSIAN 98 [21] and SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) codes [22–25]. Gaussian 98 calculations were performed using the quadratic convergence approach with the hybrid B3LYP functional [26] using a guess

function generated with the Jaguar 4.1 code [27]. We have employed a triple-ζ all electron gaussian basis set for the iron atoms and a double-ζ basis set for the other elements proposed by Schaefer et al. [28,29]. In the case of the SIESTA code, the generalized-gradient approximation (GGA) functional [30] proposed by Perdew, Burke and Erzernhof [30] was employed and pseudopotentials were generated according to the procedure of Trouiller and Martins [31] (see [14] for a more detailed description). We have used a numerical basis set of triple-ζ quality with polarization functions for the iron atoms and a double-ζ one with polarization functions for the main group elements. The values of 50 meV for the energy shift and 250 Ry for mesh cutoff, provide a good compromise between accuracy and computer time required to estimate the exchange coupling constants according to a previous study [32]. The four calculations performed, in order to obtain the three exchange coupling constants, for the model complex [Fe$_{10}$Na$_2$(O)$_6$(O-H)$_4$(O$_2$CMe)$_{10}$(chp)$_6$(H$_2$O)$_2$], replacing the phenyl by methyl groups correspond to the high spin solution ($S = 25$), two solutions with $S = 0$ (Fe2, Fe3, Fe7, Fe8, Fe9 and Fe3, Fe5, Fe6, Fe7, Fe9, respectively, with spin down), and one in which only the Fe4 and Fe9 atoms have spin down ($S = 15$).

4. Conclusions

The use of theoretical methods based on density functional theory provides a detailed knowledge of the exchange interactions present in the large Fe$_{10}$ systems. We have obtained basically the same trends and values found for other polynuclear Fe^{III} complexes [14–16], where the μ_3-O bridging ligands are those with largest antiferromagnetic couplings. Due to the impossibility to perform a full diagonalization of the Hamiltonian matrix, we have employed the Lanczos algorithm to obtain the energy of the lowest states for different values of

the total spin. The presence of spin frustration in this molecule is responsible for very tiny energy differences between the states. Hence, the S value of the ground state is extremely sensitive to the exchange coupling constants, thus, a very small change of the J values could modify the total spin of the molecule. Consequently, all simulations and fittings to obtain the J values must be done carefully for these systems with spin frustration. Even in the case of the fitting procedures, the total spin of the ground state must be verified to be sure that it is correctly reproduced.

Acknowledgements

References

[1] J.S. Miller, M. Drillon (Eds.), Magnetism, Molecules to Materials, vol. 1–5, Wiley-VCH, Weinheim, 2001–2005.

[2] D. Gatteschi, Angew. Chem. Int. Ed. 42 (2003) 246.

[3] A. Caneschi, D. Gatteschi, R. Sessoli, A.L. Barra, L.C. Brunel, M. Guillot, J. Am. Chem. Soc. 113 (1991) 5873.

[4] C. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K. Wieghardt, D. Hanke, Inorg. Chem. 32 (1993) 3099.

[5] A.L. Barra, D. Gatteschi, R. Sessoli, Chem. Eur. J. 6 (2000) 1608.

[6] S. Parsons, G.A. Solan, R.E.P. Winpenny, C. Benelli, Angew. Chem. Int. Ed. (1996) 1825.

[7] C. Benelli, J. Cano, Y. Journaux, R. Sessoli, G.A. Solan, R.E.P. Winpenny, Inorg. Chem. 40 (2001) 188.

[8] D.W. Boukhvalov, A.I. Lichtenstein, V.V. Dobrovitski, M.I. Katsnelson, B.N. Harmon, V.V. Mazurenko, V.I. Anisimov, Phys. Rev. B 65 (2002) 184435.

[9] M.J. Han, T. Ozaki, J. Yu, Phys. Rev. B 70 (2004) 184421.

[10] K. Park, M.R. Pederson, Phys. Rev. B 70 (2004) 054414.

[11] K. Park, M.R. Pederson, S.L. Richardson, N. Aliaga-Alcalde, G. Christou, Phys. Rev. B 68 (2003), 020405/1-05/4.

[12] D.W. Boukhvalov, E.Z. Kurmaev, A. Moewes, D.A. Zatsepin, V.M. Cherkashenko, S.N. Nemnonov, L.D. Finkelstein, Y.M. Yarmoshenko, M. Neumann, V.V. Dobrovitski, M.I. Katsnelson, A.I. Lichtenstein, B.N. Harmon, P. Kögerler, Phys. Rev. B 67 (2003) 134408.

[13] J. Kortus, C.S. Hellberg, M.R. Pederson, Phys. Rev. Lett. 86 (2001) 3400.

[14] E. Ruiz, A. Rodríguez-Fortea, J. Cano, S. Alvarez, J. Phys. Chem. Solids 65 (2003) 799.

[15] E. Ruiz, J. Cano, S. Alvarez, Chem. Eur. J. 11 (2005) 4767.

[16] E. Ruiz, J. Cano, S. Alvarez, Polyhedron (in press).

[17] E. Ruiz, Struct. Bond. 113 (2004) 71.

[18] G. Rajaraman, J. Cano, E.K. Brechin, E.J.L. McInnes, Chem. Commun. (2004) 1476.

[19] F. Chatelin, Eigenvalues of Matrices, Wiley, Chichester, 1993.

[20] D.P. Landau, K. Binder, Cambridge University Press, Cambridge, 2000, p. 250.

[21] M.J. Frisch et al., Gaussian 98 (Revision A.7), Gaussian, Inc., Pittsburgh, PA, 1998.

[22] D. Sánchez-Portal, P. Ordejón, E. Artacho, J.M. Soler, Int. J. Quantum Chem. 65 (1997) 453.

[23] J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, J. Phys.: Condens. Matter 14 (2002) 2745.

[24] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, J.M. Soler, Phys. Stat. Sol. A 215 (1999) 809.

[25] E. Artacho, J.D. Gale, A. García, J. Junquera, R.M. Martin, P. Ordejón, D. Sánchez-Portal, SIESTA 1.3, 2001.

[26] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[27] Jaguar 4.1, Schrödinger, Inc., Portland, 2000.

[28] A. Schaefer, H. Horn, R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571.

[29] A. Schaefer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829.

[30] J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[31] N. Trouiller, J.L. Martins, Phys. Rev. B 43 (1991) 1993.

[32] E. Ruiz, A. Rodríguez-Fortea, J. Tercero, T. Cauchy, C. Massobrio, J. Chem. Phys. 123 (2005) 074102.